TIME-DEPENDENT WAVE PACKET STUDIES OF DISSOCIATIVE RECOMBINATION AND DISSOCIATION EXCITATION

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Previously we have demonstrated that a quantum wave packet method can provide accurate predictions of cross sections for dissociative recombination (DR) [1]. We use a completely *ab initio* approach in which the resonance positions and widths are obtained as functions of the internuclear separation by carrying out accurate electron scattering calculations using the complex Kohn method. This information is then used as input to a wave packet calculation for the dissociation dynamics.

An outgrowth of this work was the development of a new mechanism for dissociative excitation (DE) of molecular ions via the autoionizing resonances. This mechanism produces dissociation at collision energies below the excitation threshold for the ion's dissociative states and can alter the dissociation products. This makes DE substantially more probable in low temperature plasmas, becoming comparable to DR. We have adapted our wave packet method to include this channel following the prescription defined by McCurdy and Turner [2] in their study of resonant enhanced vibrational excitation. The transition matrix element, T, is defined in the time-dependent boomerang approximation by:

$$T_{v_f,v_i}(E) = -\frac{i}{\hbar} \int_0^\infty e^{iEt} \left\langle \chi_{v_f}(R) \left| \frac{\Gamma(R)}{2\pi} \right| \Psi_{v_i}(R,t) \right\rangle dt$$

for the transition between an initial vibrational state with wave function $\chi_{v_i}(R)$ and $\chi_{v_f}(R)$, the final vibrational wave function of the ion. If v_f is a bound state, this describes resonant enhanced vibrational excitation; for a continuum state, this describes DE.

A time dependent wave packet is created when the incoming electron is captured into the resonance state. Its wave function satisfies the time dependent Schrödinger equation for motion on the resonance potential, $V_{res}(R) = E_{res}(R) - i\Gamma(R)/2$. The real part of the potential is the R-dependent resonance energy and $\Gamma(R)$ is its total autoionization width. The initial condition for the wave packet is given by

$$\Psi_{v_i}(R, t = 0) = (\Gamma(R)/2\pi) \; \chi_{v_i}(R).$$

In figure 1 we show the calculated DE cross sections for ^{4}HeH$^+$ and ^{3}HeD$^+$ between 5 and 25 eV. The total cross section, which contains contributions from the several resonances noted, agrees well with the measurements by Strömholm *et al*. [3]
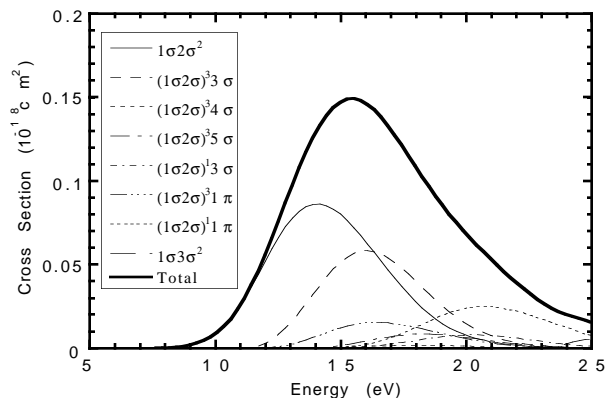

Figure 1: Total and partial resonant DE cross sections for ground state HeH$^+$ as a function of incident electron energy.

We are currently extending this method to the case of a triatomic system, D$_3^+$ where two nuclear degrees of freedom must be included to correctly describe the dissociation dynamics. The method used is similar to that employed to calculate the DR cross section for H$_3^+$, but now includes the DE resonant mechanism.

In addition, we are studying the DR final state fragment distributions. In the absence of coupling between the final state potential surfaces, the distributions can be predicted after the autoionization width goes to zero. However in the case of HeH$^+$ the lowest resonance state correlates asymptotically to the ion-pair state. Therefore it crosses all the Rydberg states before dissociating. The coupling between the ion pair state and the Rydbergs must be included in the wave packet dynamics to allow the final state distribution to be determined.

References
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3. C. Strömholm *et al.*, Phys. Rev. A **54**, 3086 (1996).